

Surface-Tension Properties of Some Polydispersed Alkyl-Substituted Polyoxyethylated Phenylsulfonamides

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ABSTRACT: Twenty-nine laboratory-prepared polydisperse nonionic surfactants, derived from polyoxyethylated *N*-alkylphenylsulfonamides [$R\phi SO_2N(R')(EO)_nH$], have been characterized. EO is ethoxylation; *R* is hydrogen, *n*-butyl or *t*-butyl; *R'* is hexyl, octyl, or decyl; and $(EO)_n$ is varied from $(EO)_4$ to $(EO)_{20}$. Surface tension in aqueous solution was studied. The critical micelle concentration, surface excess, minimum area per molecule, effectiveness of surface-tension reduction, and free energy of micelle formation were calculated from the surface-tension measurements. The critical micelle concentrations for the derivatives in which *R'* = hexyl were considerably higher than the corresponding derivatives where *R'* is octyl or decyl. The greatest surface-tension reduction was found in the *R'* = *n*-octyl derivatives where *R* is *t*-butyl with $(EO)_9$ or *n*-butyl with $(EO)_{11}$.

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Articles (1,2) have pointed out that the surfactant industry has assorted products for different uses. This is because surfactants are usually tailor-made or adapted to solve specific needs. In agriculture, surfactants are needed primarily to solubilize and disperse pesticide compounds and to aid in better pesticide penetration into the foliage. A lesser known agricultural use for surfactants is as soil conditioners (3), which function primarily as wetting agents to increase water penetration into soil.

We chose to study nonionic surfactants, specifically ethoxylates, rather than anionics, cationics, or amphoterics because nonionics are nontoxic to plants (4), low in price, low foaming, easy to work with, and established wetting agents. This research is part of an overall plan to obtain information that will lead to the development of an inexpensive, efficient soil wetting agent to increase soil water infiltration and help control soil erosion.

In previous research, two soil components, sand and kaolin, were treated with some of the compounds discussed in this paper to determine surfactant adsorption characteristics in soil (5). To understand more completely the mechanism of surfactant adsorption, it is important to determine the

surfactant properties of each polydisperse compound and especially how molecular structure affects the surfactant properties. In the past, surfactant soil adsorption was not studied from the standpoint of surfactant molecular structure; only the surfactant type—anionic, cationic, nonionic, or amphoteric—was considered. The research here provides data about the effect of surfactant structure on aqueous solution properties that may be used to interpret the adsorption mechanism of these phenylsulfonamide surfactants onto soil.

EXPERIMENTAL PROCEDURES

Materials. The phenylsulfonamide derivatives were prepared by a co-worker in our laboratory, and their synthesis and wetting properties were described in a previous publication (6). The derivatives were mixtures of polydisperse compounds where *n* = average ethoxylation (EO), and all were liquid at room temperature. Distilled water was used for the solutions. Ethanol was of ACS grade.

Methods. The surface-tension measurements were made with a duNouy ring type tensiometer, Fisher model 21, automatic shut-off type (Fisher Scientific, Pittsburgh, PA). Surfactant solutions were aged for two hours before any measurements were made. Three readings were made on each sample to determine any changes with time and to obtain an average value. Surface-tension data were corrected for ring size. Surface tension vs. surfactant concentration was plotted on a semi-log scale, and the critical micelle concentration (CMC) was obtained as the point of intersection of the two straight lines. The surface excess (Γ), area/molecule adsorbed at the interface (*A*), and the standard free energy of micelle formation (ΔG°_m) were calculated by the methods described by Rosen *et al.* (7) and Rosen and Zhao (8). The range of surfactant concentrations studied was normally 10–1000 mg/L. All measurements were made at room temperature $23 \pm 2^\circ\text{C}$. Distilled water and ethanol were used as surface-tension standards. The hydrophile–lipophile balance (HLB) was calculated as $HLB = \% EO/5$.

RESULTS AND DISCUSSION

In the previous report (6), optimum wetting properties were found for ethoxylate adducts with 5–10 EO units. This EO

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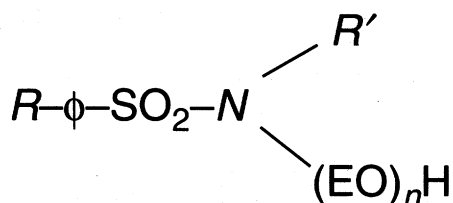


FIG. 1. Parent compound. Phenylsulfonamide structure: $R = \text{H}$, n -butyl, $tert$ -butyl; $R' = \text{C}_6$, C_8 , C_{10} (straight chain); $N = 4$ to 20.

chainlength corresponded to cloud points of 25°C, HLB values of 10–12, and minimal surface tensions. Surface tension decreased as R' was increased, and reached a minimum for $R' = \text{octyl}$ or decyl . Figure 1 shows the parent compound, which is an N,N alkyl-substituted polyethoxylated phenylsulfonamide, where the number of EO groups, n , is varied from 4–20. Twenty-nine compounds derived from this structure were examined to determine what effect molecular structure has on surfactant properties. R was hydrogen, tertiary butyl, or a normal butyl group; R' was a normal hexyl, octyl, or decyl group. The EO content was varied to obtain a series of adducts with a spread in HLB values.

It is well known (9) that nonionic ethoxylate properties are a function of EO content. Moreover, solubility, surface tension, wetting time, detergency, foam height, cloud point, etc., often produce a “u”-shaped curve when plotted against EO content. A minimum in the curve is frequently found where the EO content is about 50%, i.e., an HLB = 10. This was the observed trend in the previous publication (6). In Tables 1, 2, and 3, the lower ethoxylates have poor solubility, and the higher ethoxylates are too soluble for optimum surfactant properties. It is clear that, in discussing polydisperse ethoxylated phenylsulfonamides, there is a threshold EO value that must be reached before these nonionic surfactants become reasonably soluble in water.

Figure 2 shows a typical plot of surface tension vs. surfactant concentration on a semi-logarithmic scale. A surface tension of 32 mN/m was obtained at the CMC. The plot yields a

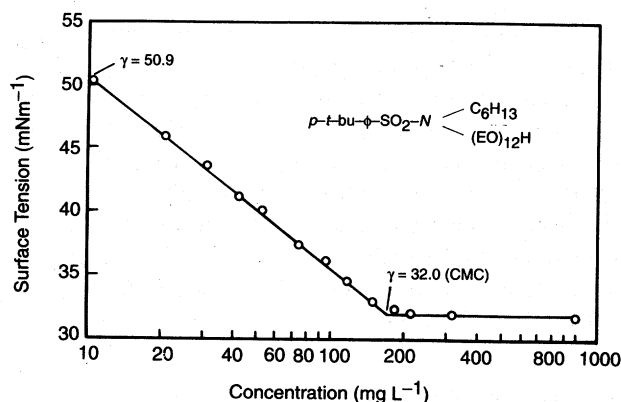


FIG. 2. Surface tension vs. surfactant concentration of polydisperse p - t -bu- ϕ -SO₂-N(C₆H₁₃)(EO)₁₂H; EO = ethoxylation.

straight line from the CMC to 10 mg/L surfactant concentration (the minimum concentration studied) and was used to calculate the surface excess by the Gibbs equation:

$$\Gamma = \frac{1}{2.30 RT} \left(\frac{-\partial \gamma}{\partial \log C} \right)_T \quad [1]$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T is absolute temperature, $(-\partial \gamma / \partial \log C)_T$ is the slope of the γ vs. $\log C$ plot at constant temperature, and Γ is the surface excess in mol/cm². The area per molecule at the interface was calculated from the surface excess by the following equation:

$$A = \frac{10^{16}}{\Gamma N} \quad [2]$$

where A is the area per molecule (nm² × 10²), and N is Avogadro's number. The standard free energy of micelle formation, ΔG°_m , was calculated from the CMC by the following equation:

$$\Delta G^\circ_m = 2.303 RT \log \text{CMC} \quad [3]$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T is the absolute temperature, and CMC is the critical micelle concentration (mol/dm³).

Tables 1, 2, and 3 list the results for the three series of polydisperse adducts studied, i.e., phenylsulfonamide, p - t -butylphenylsulfonamide and p - n -butyl phenylsulfonamide. The surface tension at 10 mg/L (γ_{10}) was used as a measure of the weight-based effectiveness of the various surfactants in surface-tension lowering. This is of concern in field applications where the cost per pound is important.

An attempt was made to relate surfactant molecular areas, determined experimentally, with surfactant areas, obtained by use of molecular models. More than likely, the polydispersity and branched-chain nature of the adducts made this unrealistic. In one case [Table 2, $R' = \text{C}_{10}$, (EO)₁₇], a molecular area of 0.32 nm² was calculated from the surface excess; this area seems highly unlikely for this adduct. Nevertheless, the areas projected onto a plane by space-filling molecular models were measured, and these areas were compared to the surface areas reported in Tables 1–3 as calculated from the surface excess. Agreement between the models and the experimentally determined areas is obtained if we assume that only the phenyl group plus the sulfonamide group and the R group contribute to the surface areas of the adsorbed species. For example, the experimentally determined areas for the $tert$ -butylphenylsulfonamide series of compounds (Table 2) vary between 0.33 and 0.75 nm² per molecule or 0.48 and 0.66 nm² if we disregard the two extreme values. With space-filling models, we obtain 0.60 nm² if we disregard the R' and the EO side chains. Including R' of C_6 increases the area by about 0.36 nm²; including (EO)₅ increases the area by about 0.72 nm². Including either of these latter contributions to the surface area gives poor agreement between space-filling models and the experimentally determined values. One possible scenario would be the t -butylphenylsulfonamide structure in the surface with the C_6 side chain above the surface and the (EO)₅ group beneath the surface.

TABLE 1

Surfactant Properties of Polydisperse Alkyl-Substituted Ethoxylated Phenylsulfonamide, ϕ -SO₂-N(R')(EO)_nH

R'	(EO) _n	MW ^a	HLB ^b	γ_{10} ^c	γ_{CMC} ^d	CMC ^e	$\Delta G^\circ m^f$	Γ^g	A ^h
C ₆ H ₁₃	6	506	10.5	61.5	36.8	2.82 (i)	-14.5	2.13	77.9
C ₆ H ₁₃	8	594	11.9	61.1	37.5	3.20 (i)	-14.2	2.33	71.3
C ₆ H ₁₃	10	682	12.9	61.2	38.8	4.40 (i)	-13.4	1.92	86.5
C ₆ H ₁₃	12	770	13.8	61.5	40.3	4.16 (i)	-13.6	1.8	92
C ₈ H ₁₇	4	445	8	Poor solubility					
C ₈ H ₁₇	8	622	11.4	51.6	33.4	2.65 (ii)	-20.4	2.56	64.9
C ₈ H ₁₇	12	798	13.3	54.8	33.4	2.88 (ii)	-20.2	2.74	60.6
C ₁₀ H ₂₁	4	474	7.5	Poor solubility					
C ₁₀ H ₂₁	6	562	9.4	37.1	32.2	3.83 (iii)	-25.2	2.27	73.1
C ₁₀ H ₂₁	8	650	10.8	41.3	33	3.85 (iii)	-25.2	3.66	45.3
C ₁₀ H ₂₁	10	737	11.9	44.4	35	5.16 (iii)	-24.5	2.85	58.3
C ₁₀ H ₂₁	12	825	12.8	47.3	37.3	6.30 (iii)	-24	2.44	68
C ₁₀ H ₂₁	14	913	13.5	49.4	38.5	6.90 (iii)	-23.7	2.56	64.9

^aMolecular weight.^bHydrophile-lipophile balance (% EO/5) where EO is ethoxylation.^cSurface tension at 10 mg L⁻¹ concentration (mNm⁻¹).^dSurface tension at critical micelle concentration (CMC) (mNm⁻¹).^eCMC (i) 10⁻³ molar, (ii) 10⁻⁴ molar, (iii) 10⁻⁵ molar.^fFree energy of micelle formation (kJ mol⁻¹).^gSurface excess (mol cm⁻² × 10⁻¹⁰).^hArea per molecule (nm² × 100).

Table 1 lists the aqueous surfactant properties of the polydispersed phenylsulfonamide adducts, where *R* is H, *R'* is hexyl, octyl, or decyl, and EO varies from 4–14. The EO variation covered a range of HLB from 7.5–13.8, with a molecular weight range of 445–913. The HLB values suggested that the hexyl derivatives would reduce the surface tension considerably. However, as can be seen from the surface tension values at 10 mg/L (γ_{10}), these derivatives caused a reduction of only ~10 mN/m (61.1).

In a previous publication (6), the Draves test, which measures the time (in seconds) required for a weighted cotton skein to sink in 0.1% surfactant solution, showed that the phenylsulfonamide hexyl adducts had long wetting times. The shortest wetting time for any of the hexylphenylsulfonamide adducts was 50 s, whereas a wetting time of 25 s or preferably less is desired (10).

The octyl adducts, listed in Table 1, had better surfactant properties than the hexyl adducts, but the decyl adducts had the best surfactant properties overall as measured by the reduction in surface tension at γ_{10} and at the CMC γ_{CMC} . The CMC of the decyl adduct (3.83×10^{-5} molar) is about one order of magnitude less than the comparable octyl adduct. The decyl adducts demonstrate how increasing EO content decreases surfactant properties overall. The γ_{10} surface tension for the decyl adduct increased from 37.1 to 49.4 as EO was varied from (EO)₆ to (EO)₁₄, and γ_{CMC} increased from 32.2 to 38.5. Thus, there was no further surface-tension decrease with EO of any adduct past the point of “full solubility” at (EO)₆. The 8th column, $\Delta G^\circ m$, shows the decyl adducts with the larger negative values as compared to the hexyl and octyl derivatives. Even at a surfactant concentration of 0.1% (1000 mg L⁻¹), the CMC had not been reached for hexyl adducts. Thus, the $\Delta G^\circ m$ value for the hexyl deriv-

atives was made at higher concentrations. The surface excess (Γ) and area per molecule (*A*) were calculated the usual way (7,8). It can be seen that, as the EO content is increased for the hexyl adducts, the area per molecule also increases, in agreement with the literature (10). The octyl and decyl adducts, however, have smaller areas per molecule and do not follow this trend. This suggests that EO may not determine the surface area of these adducts. Table 1 shows that the decyl adducts have good surfactant properties, while the hexyl adducts are too soluble to be good surfactants. From γ_{10} , we observe how changing molecular structure changes the surfactant properties for the same surfactant weight, 10 mg L⁻¹. Comparing the adduct in Table 1, where (EO)_n = 8, we see that the γ_{10} values for the hexyl, octyl, and decyl adducts decrease from 61.1, to 51.6, to 41.3, and the CMC decreases by an order of magnitude from the hexyl to the octyl to the decyl adduct. Each methylene group added to the hydrophobic part of the molecule lowers the CMC threefold (11); thus two methylenes would cause a ninefold decrease in the CMC, approximately what we observed. Also $\Delta G^\circ m$ decreased from about -13 to -25 k J/mole in going from the hexyl to the decyl adduct.

The effect of molecular structure on surfactant properties, when a tertiary butyl group is introduced into the benzene ring at *R*, is shown in Table 2. In Table 1, where *R* = H, the hexyl adducts were shown to be soluble and poor surfactants, but in Table 2, where *R* = *t*-butyl, the hexyl adducts exhibit good surfactant properties. This is undoubtedly due to the overall increase in the hydrophobicity of the molecule. The hexyl adducts in this Table, in terms of total carbon content, compare most closely with the unsubstituted octyl adducts in Table 1, when one considers the nonpolar content of the molecules. They also have similar $\Delta G^\circ m$ values. Both the octyl

TABLE 2

Surfactant Properties of Polydisperse Alkyl-Substituted Ethoxylated *p*-*t*-butyl Phenylsulfonamide, *p*-*t*-bu- ϕ -SO₂-N(R') (EO)_nH^a

R'	(EO) _n	MW	HLB	γ_{10}	γ_{CMC}	CMC	$\Delta G^\circ m$	Γ	A
C ₆ H ₁₃	7	606	10.2	43.5	31.5	1.57 (i)	-21.7	2.21	75.1
C ₆ H ₁₃	9	694	11.5	47.8	31.4	1.95 (i)	-21.2	2.5	66.4
C ₆ H ₁₃	12	826	12.8	50.9	32	2.06 (i)	-21	2.68	61.9
C ₆ H ₁₃	14	914	13.5	53.6	32.4	2.30 (i)	-20.8	2.85	58.3
C ₈ H ₁₇	5	546	8.1	Poor solubility					
C ₈ H ₁₇	9	722	11	36.4	30.4	3.19 (ii)	-25.7	2.85	58.3
C ₈ H ₁₇	15	986	13.4	43	30.8	5.78 (ii)	-24.2	2.8	59.3
C ₈ H ₁₇	19	1162	14.4	45.6	31.4	5.34 (ii)	-24.4	3.14	52.9
C ₁₀ H ₂₁	5	574	7.7	Poor solubility					
C ₁₀ H ₂₁	9	750	10.6	44	31.3	6.00 (ii)	-24.1	3.49	47.8
C ₁₀ H ₂₁	13	926	12.4	38.6	30.6	3.56 (ii)	-25.4	2.78	59.7
C ₁₀ H ₂₁	17	1102	13.6	53.7	30.6	5.99 (ii)	-24.1	5.06	32.8

^aSee Table 1 for all abbreviations and explanations.

and decyl adducts in Table 2 have surfactant properties similar to the decyl adducts in Table 1, as shown mainly by the $\Delta G^\circ m$ values. The best surfactant in Table 2, as shown by γ_{10} , γ_{CMC} , and $\Delta G^\circ m$, is the octyl adduct with (EO)_n = 9. This adduct had the lowest surface tension and also the most negative $\Delta G^\circ m$. Previous studies (6) showed that it had a Draves wetting time of 20 s.

The effect on surfactant properties when a normal butyl group is substituted into the benzene ring at R is shown in Table 3. The results for the *n*-butyl octyl adducts are not too different from the *t*-butyl octyl adducts in Table 2. The best surfactant in Table 3 is the (EO)_n = 11 adduct, as indicated by γ_{10} , γ_{CMC} , and $\Delta G^\circ m$. The molecular surface areas are somewhat larger, possibly due to the longer straight chainlength of the *n*-butyl group at the surface, compared to the tertiary butyl group. The *n*-butyl group increases the length of the molecule and the overall rectangular cross-sectional area.

In conclusion, we found that, for the polydispersed alkyl-substituted polyethoxylated phenylsulfonamides, increasing EO enhanced solubility in water, and that the surfactant properties of the molecule usually decreased with further ethoxylation. Adding EO groups generally raised the CMC and gave a less negative $\Delta G^\circ m$ value. Increasing EO content tended to make interfacial molecular areas larger only for the hexyl derivatives of phenylsulfonamides (12). Alkyl substitution at R affected surfactant properties beneficially due to increased total carbon in the hydrophobic part of the molecule. Thus, the *t*-butyl adduct with a hexyl side chain at R' had properties similar to the unsubstituted phenyl adduct with the octyl side

chain at R' with the same degree of ethoxylation. Alkyl substitution at R' showed the most marked surfactant effect. Solubility, surface tension, and CMC values all decreased from hexyl to octyl, and greater negative values for the $\Delta G^\circ m$ were observed for the octyl adduct. We concluded that, of the preparations studied here, those with a tertiary butyl or normal butyl at R and an octyl group at R' with nine or eleven ethoxyl groups were the most efficient in lowering the surface tension and would be expected to make good wetting agents.

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TABLE 3

Surfactant Properties of Polydisperse Alkyl-Substituted Ethoxylated *p*-*n*-butyl Phenylsulfonamide, *p*-*n*-bu- ϕ -SO₂-N(R') (EO)_nH^a

R'	(EO) _n	MW	HLB	γ_{10}	γ_{CMC}	CMC	$\Delta G^\circ m$	Γ	A
C ₈ H ₁₇	7	633	9.7	Poor solubility					
C ₈ H ₁₇	11	809	12	36.1	30.6	3.34	-25.5	2.21	75.1
C ₈ H ₁₇	15	986	13.4	42.5	31.2	5.58	-24.3	2.68	62
C ₈ H ₁₇	20	1205	14.6	44.8	30.6	7.05	-23.7	2.62	63.3

^aSee Table 1 for all abbreviations and explanations.

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